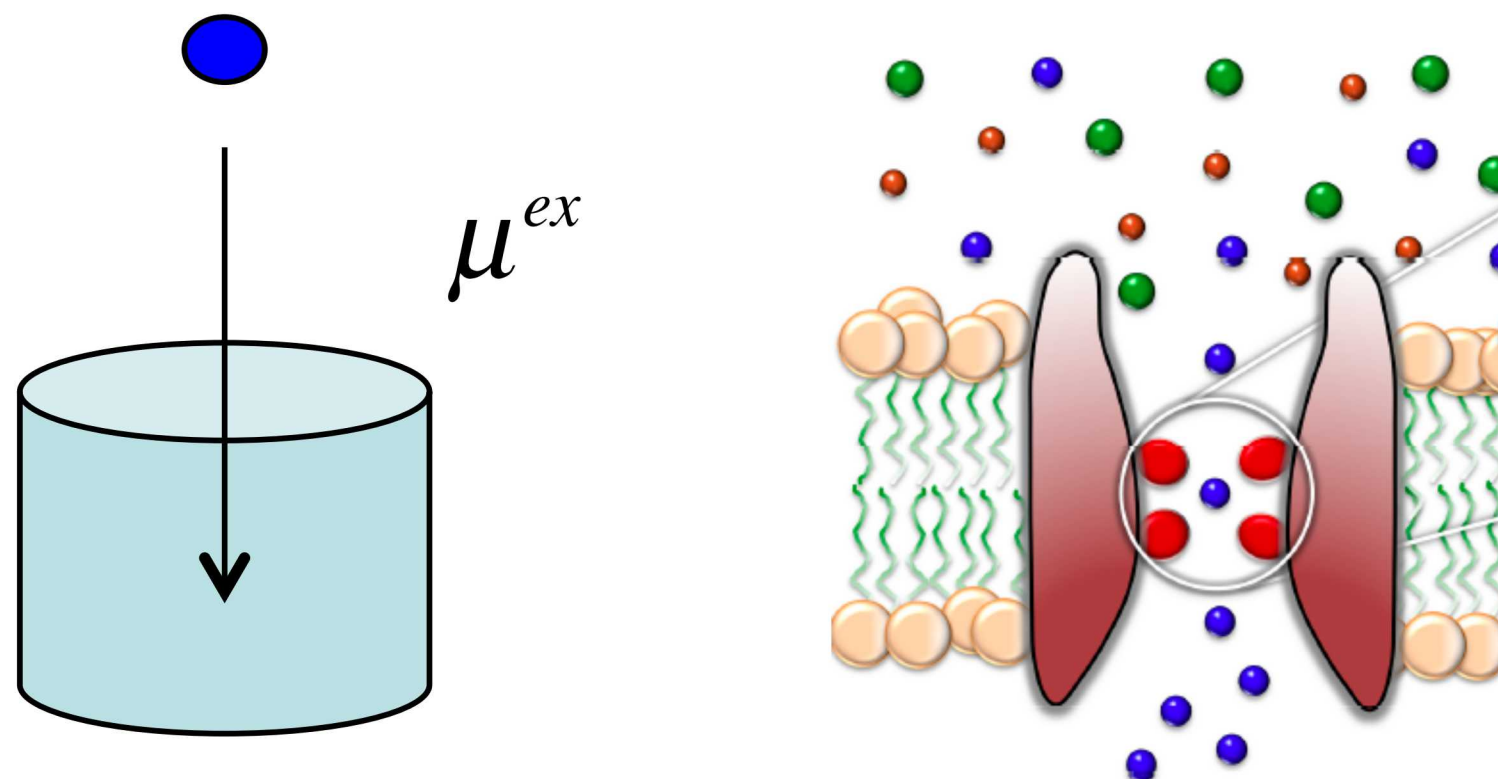


Assessing Dispersion & Exchange Corrected DFT for Ion Hydration

Marielle Soniat, David Rogers, Susan Rempe



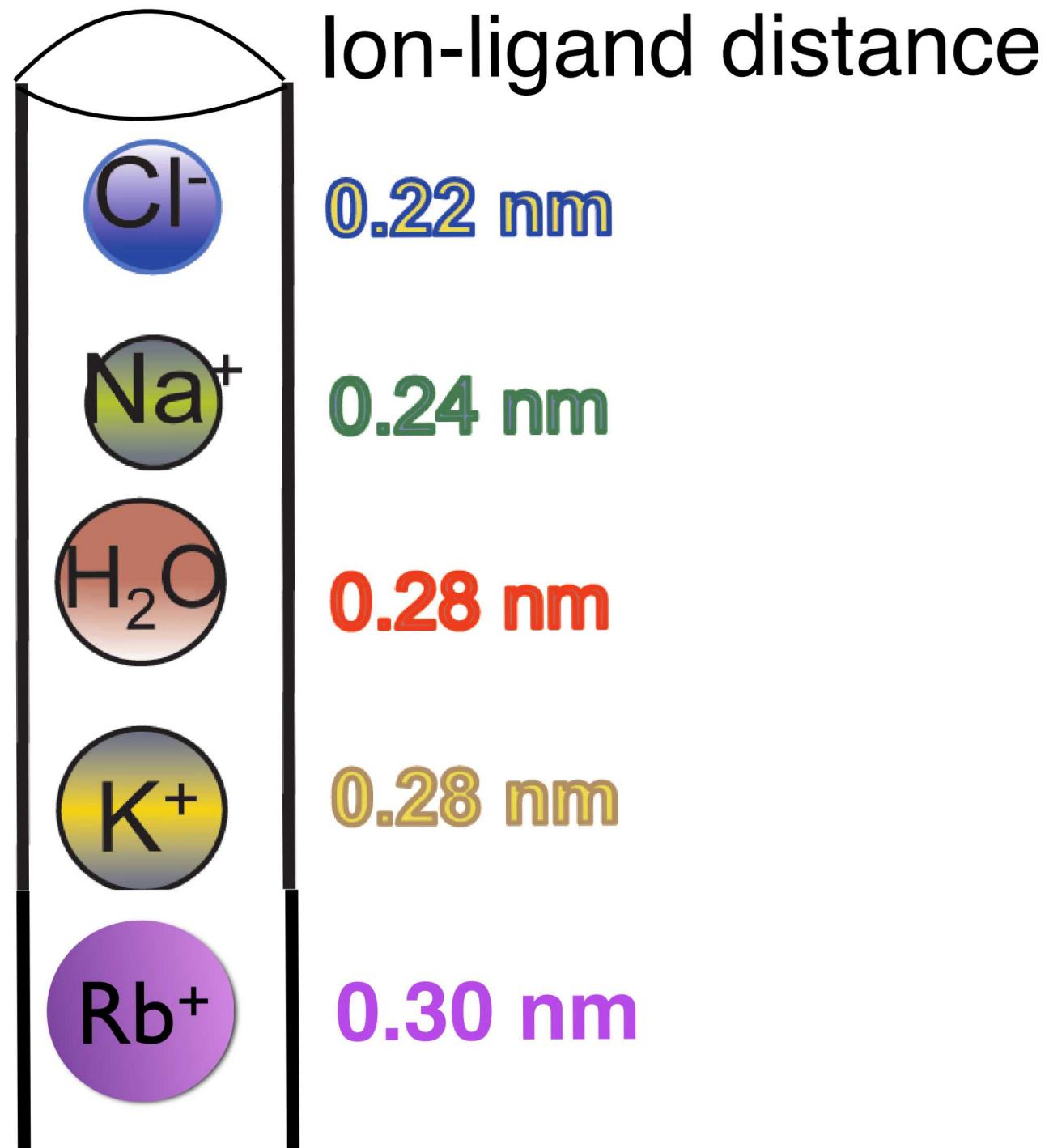
Sandia Mountain



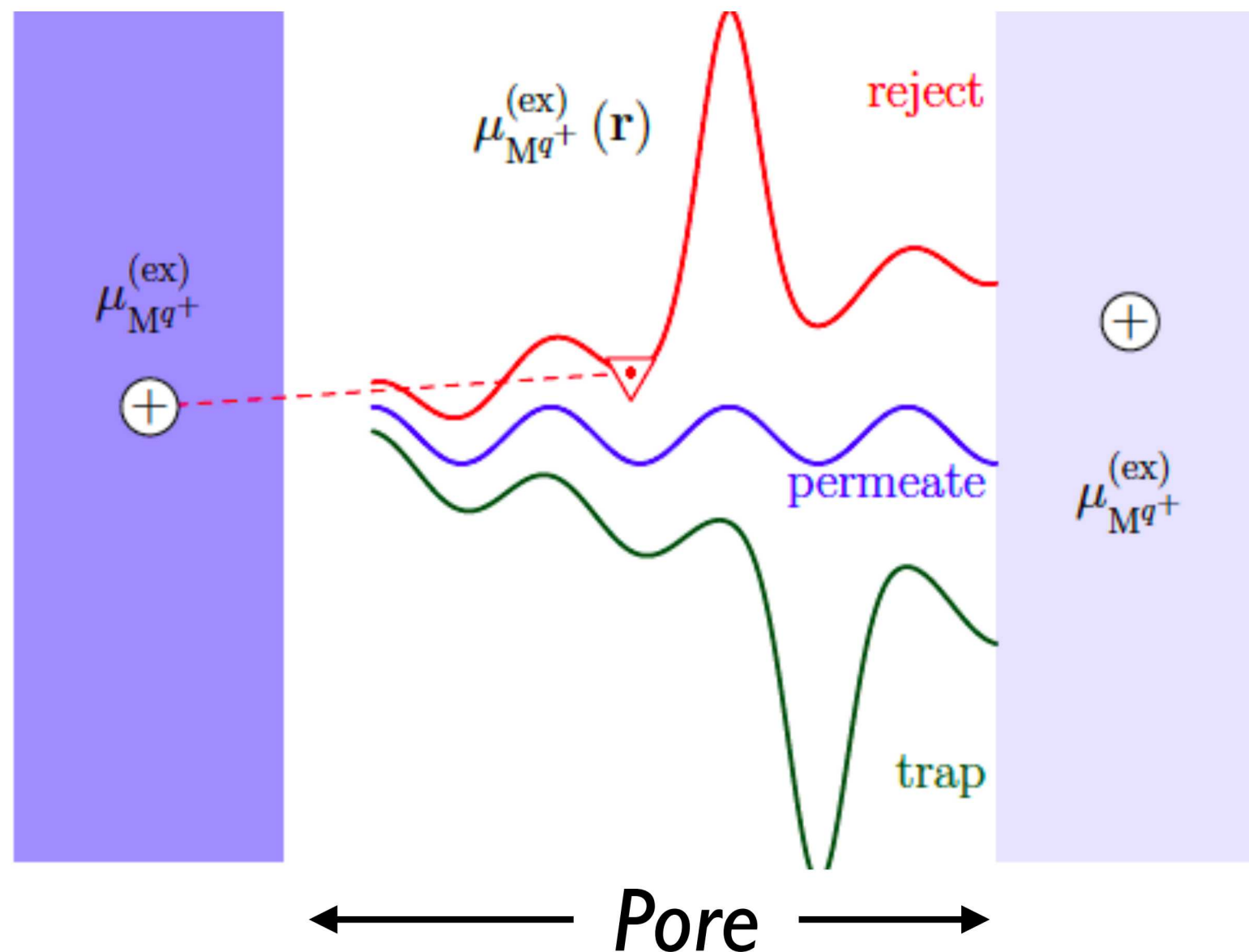
Albuquerque, NM



Challenge: Separating similar sizes



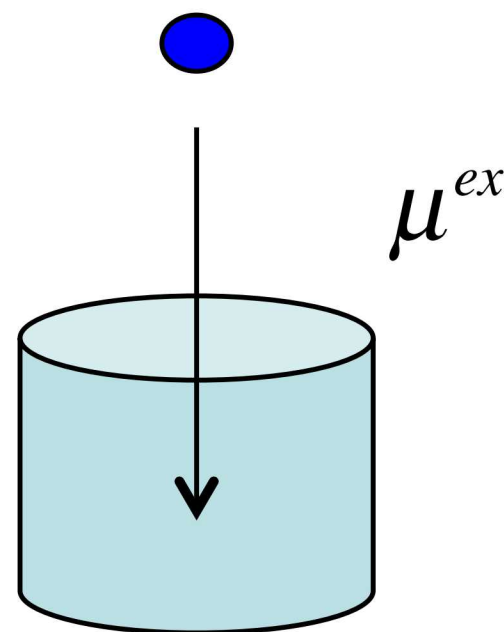
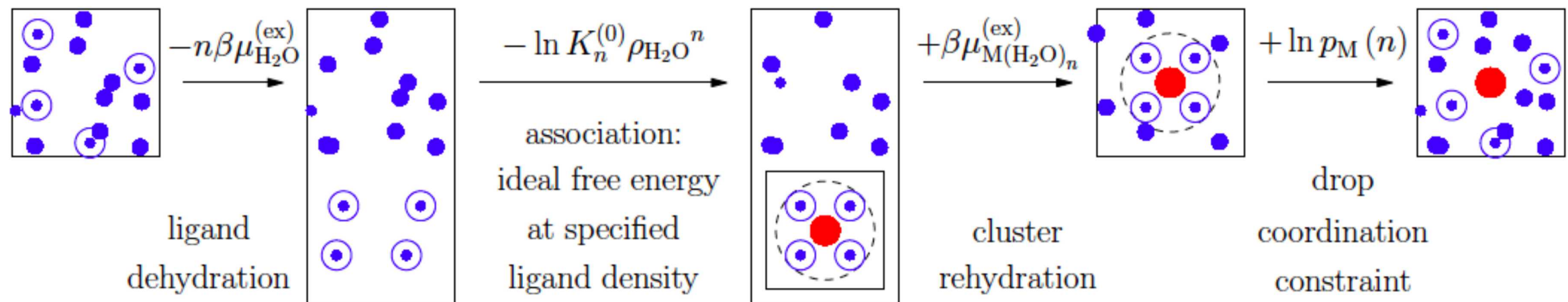
Challenge: Free energy of translocation



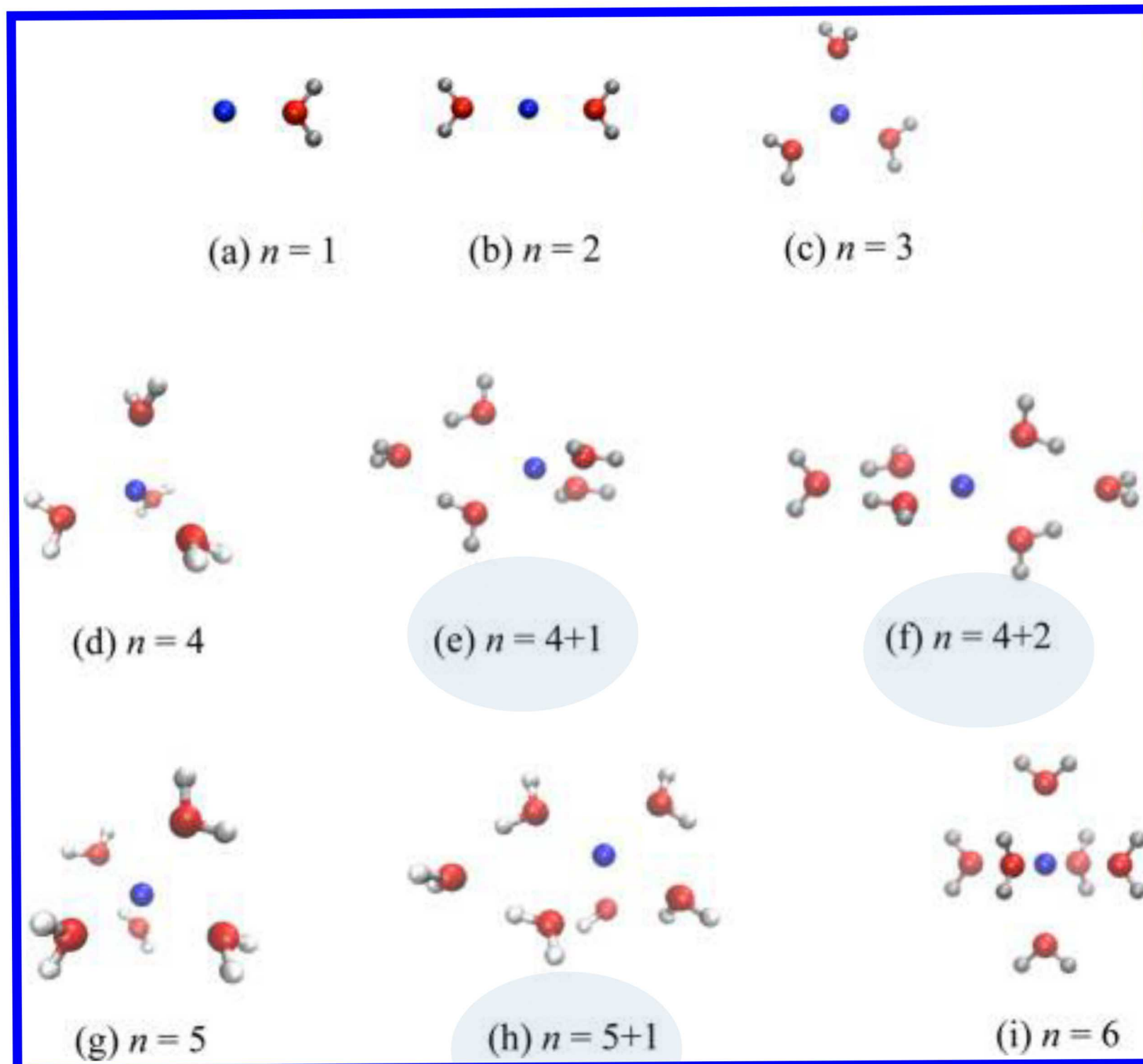
- **Keys:** specific pore size, chemistry, ligand number?

Challenge: Free energy of hydration

Gas-phase DFT



Na-water clusters



Density functionals tested

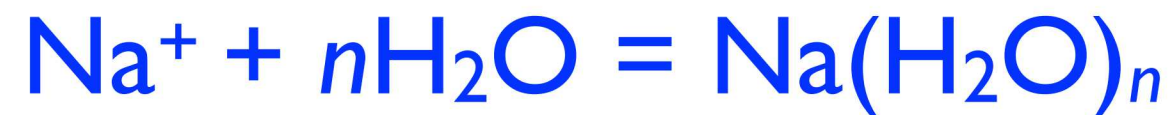
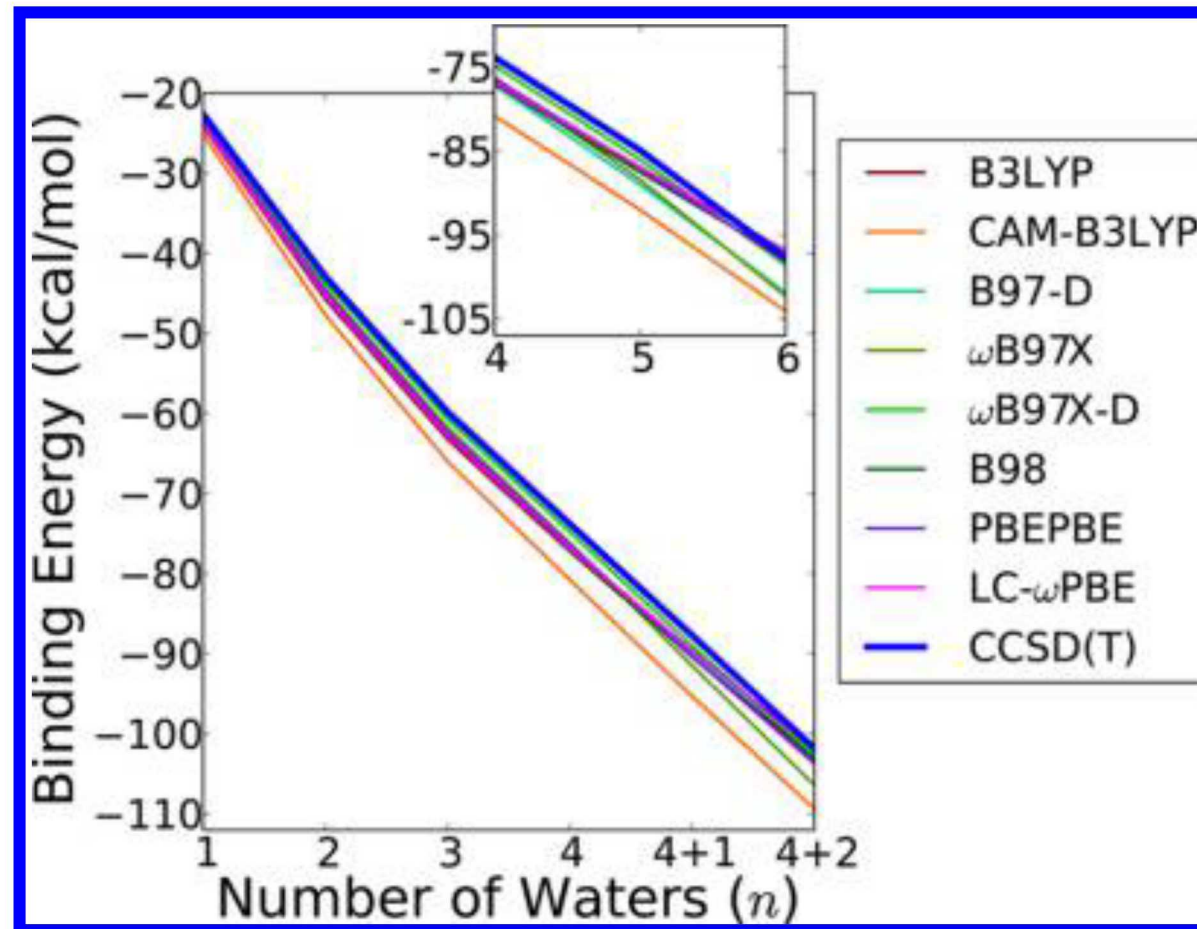
e⁻ correlation

$$C_{ij}^6/r_{ij}^6$$

exchange
e⁻ delocalization

- Generalized gradient approx. (PBE, PBE)
- Hybrid GGA (B98, B3LYP)
- Dispersion-corrected hybrid GGA (B97-D)
- Range-separated GGA (LC-PBE, CAM-B3LYP, ω B97X)
- Combined range-separation & dispersion corrected (ω B97X-D)

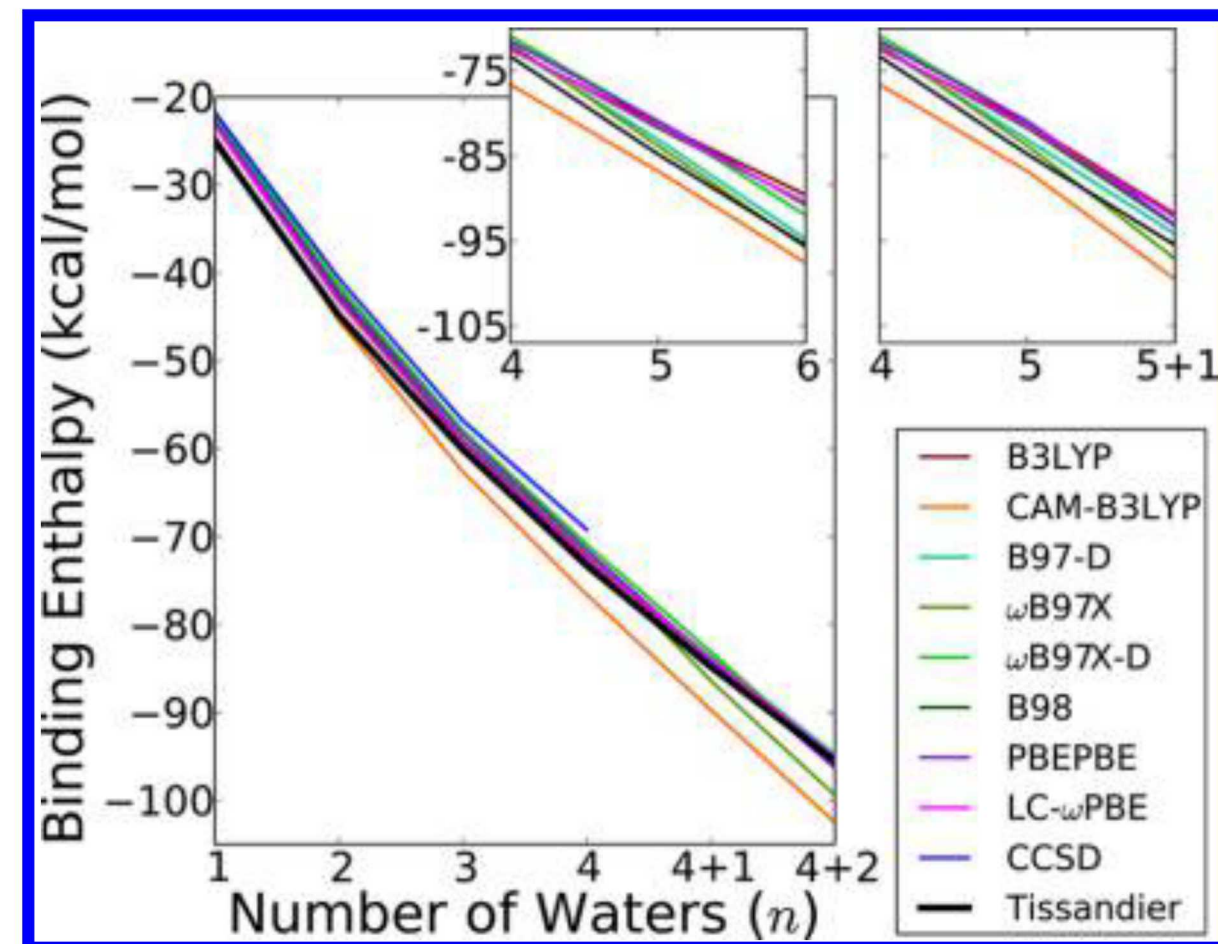
Cluster formation energies



Cluster enthalpies

	CCSD MAE(4)	Tissandier	
		MAE(4)	MAE(6,ss)
B3LYP	3 (1)	1 (1)	1 (1)
CAM-B3LYP	5 (2)	2 (1)	3 (2)
B97-D	2 (1)	2 (1)	2 (1)
ω B97X	2 (1)	2 (1)	2 (1)
ω B97X-D	1 (1)	3 (1)	2 (1)
B98	2 (1)	2 (1)	1 (1)
PBEPBE	2 (1)	2 (0.4)	2 (1)
LC- ω PBE	2 (1)	1 (1)	1 (1)
CCSD		4 (0.5)	

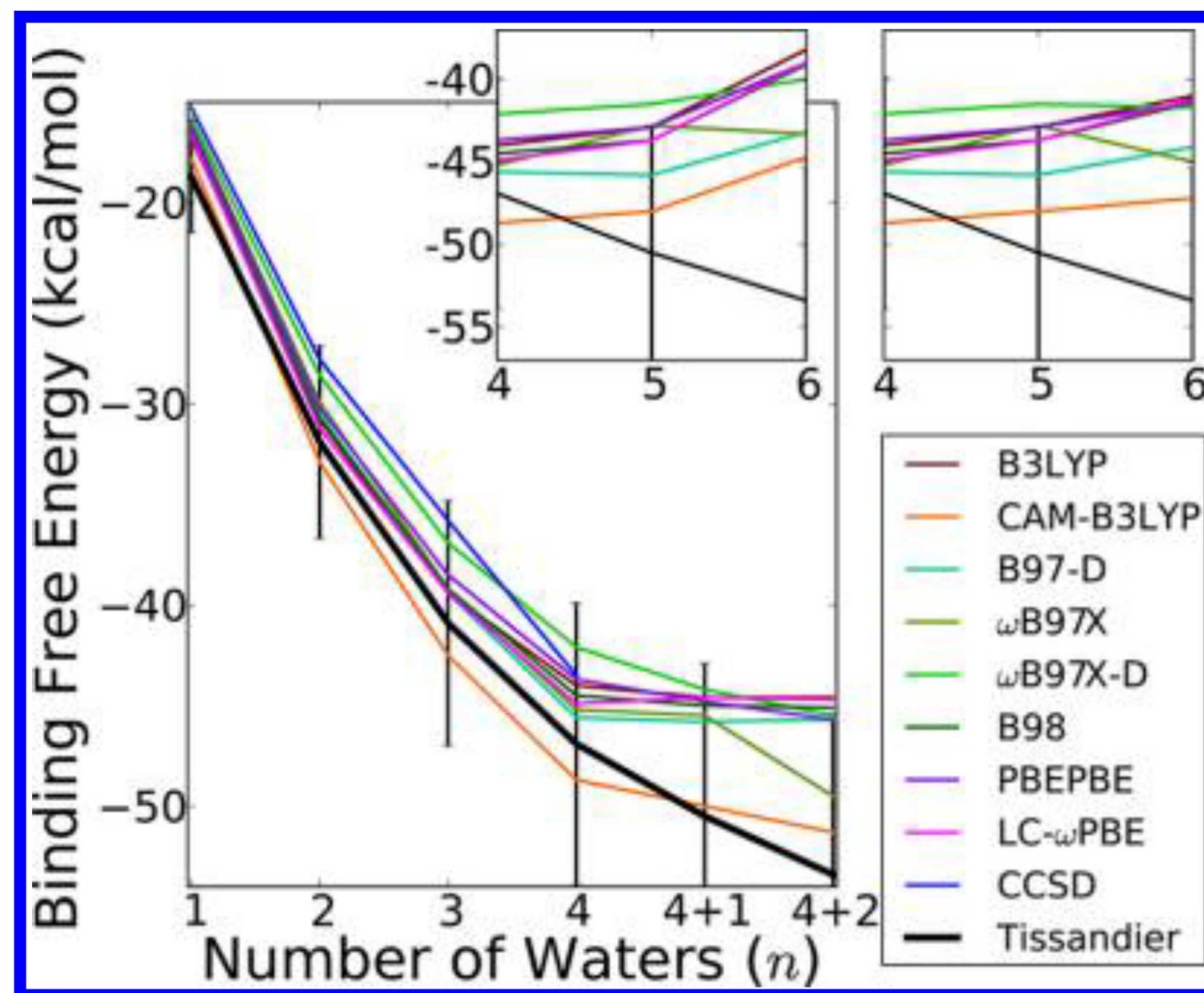
^aUnits are kcal/mol.



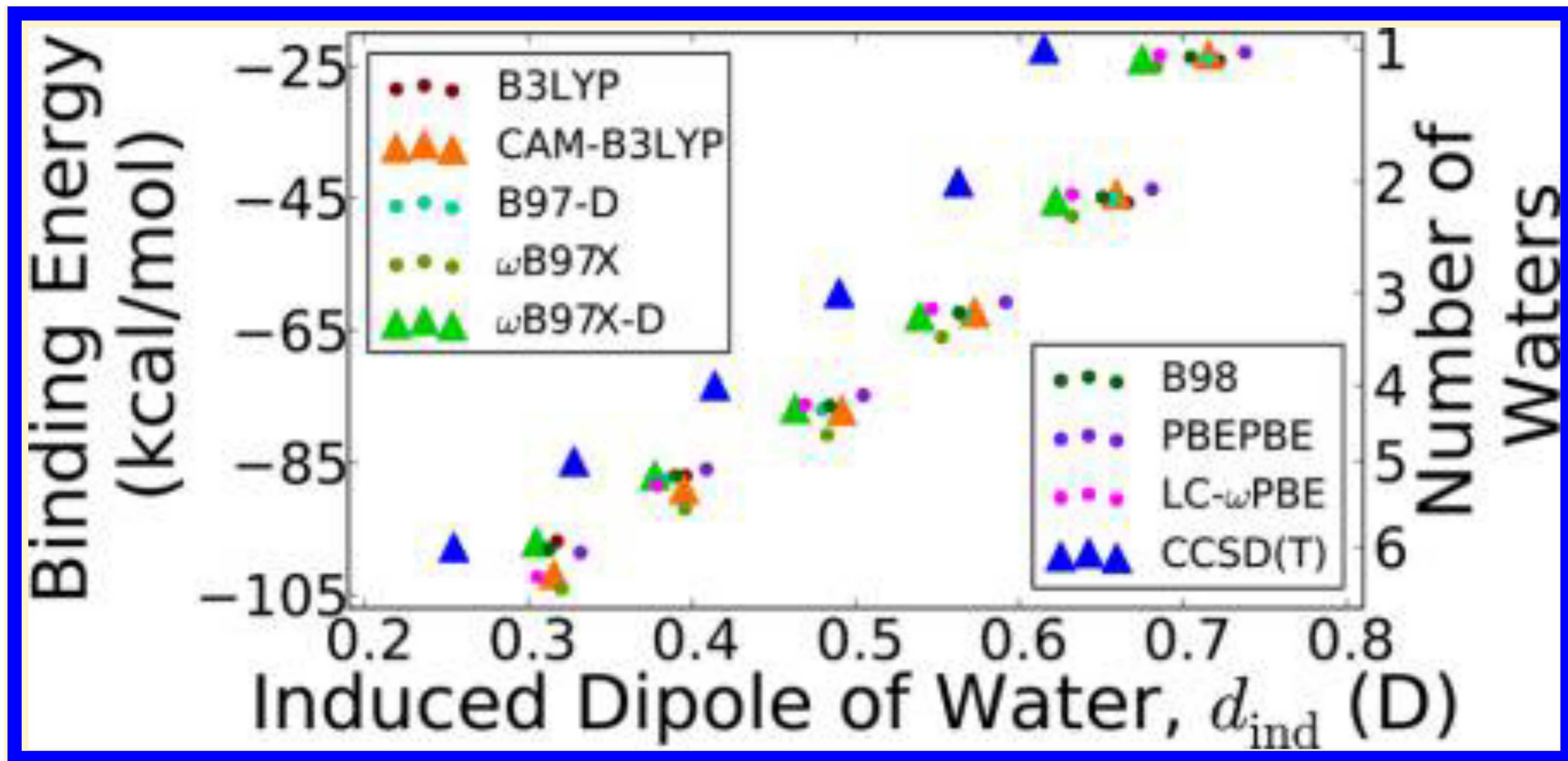
Cluster free energies

	CCSD MAE(4)	Tissandier	
		MAE(4)	MAE(6,ss)
B3LYP	2 (1)	2 (1)	4 (3)
CAM-B3LYP	5 (2)	1 (0.4)	1 (1)
B97-D	2 (1)	2 (1)	3 (3)
ω B97X	2 (1)	2 (0.4)	3 (1)
ω B97X-D	1 (0.4)	4 (1)	5 (2)
B98	2 (1)	2 (1)	4 (3)
PBEPBE	2 (1)	2 (1)	4 (2)
LC- ω PBE	2 (1)	2 (1)	3 (3)
CCSD		4 (1)	

^aUnits are kcal/mol.



Ion-induced dipoles

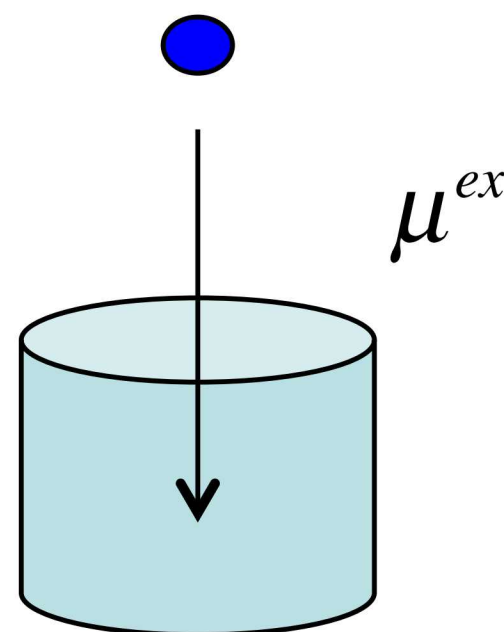
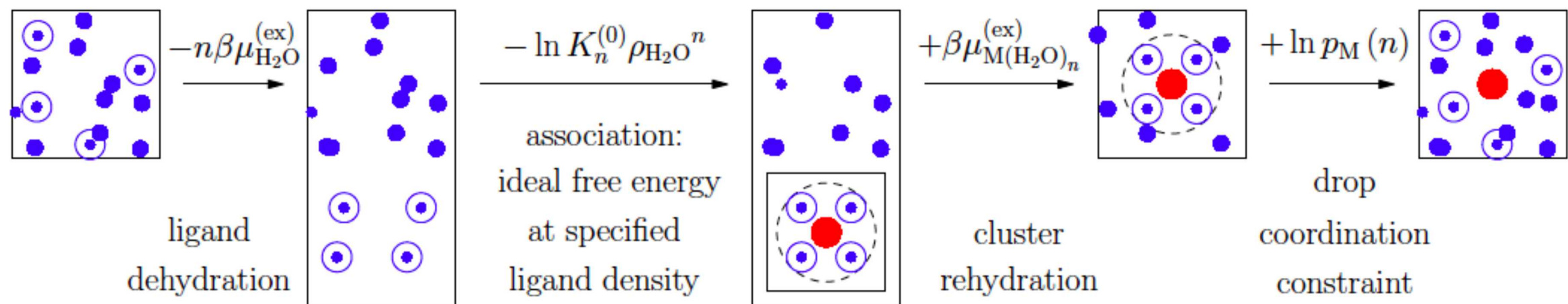


Challenge: Free energy of hydration

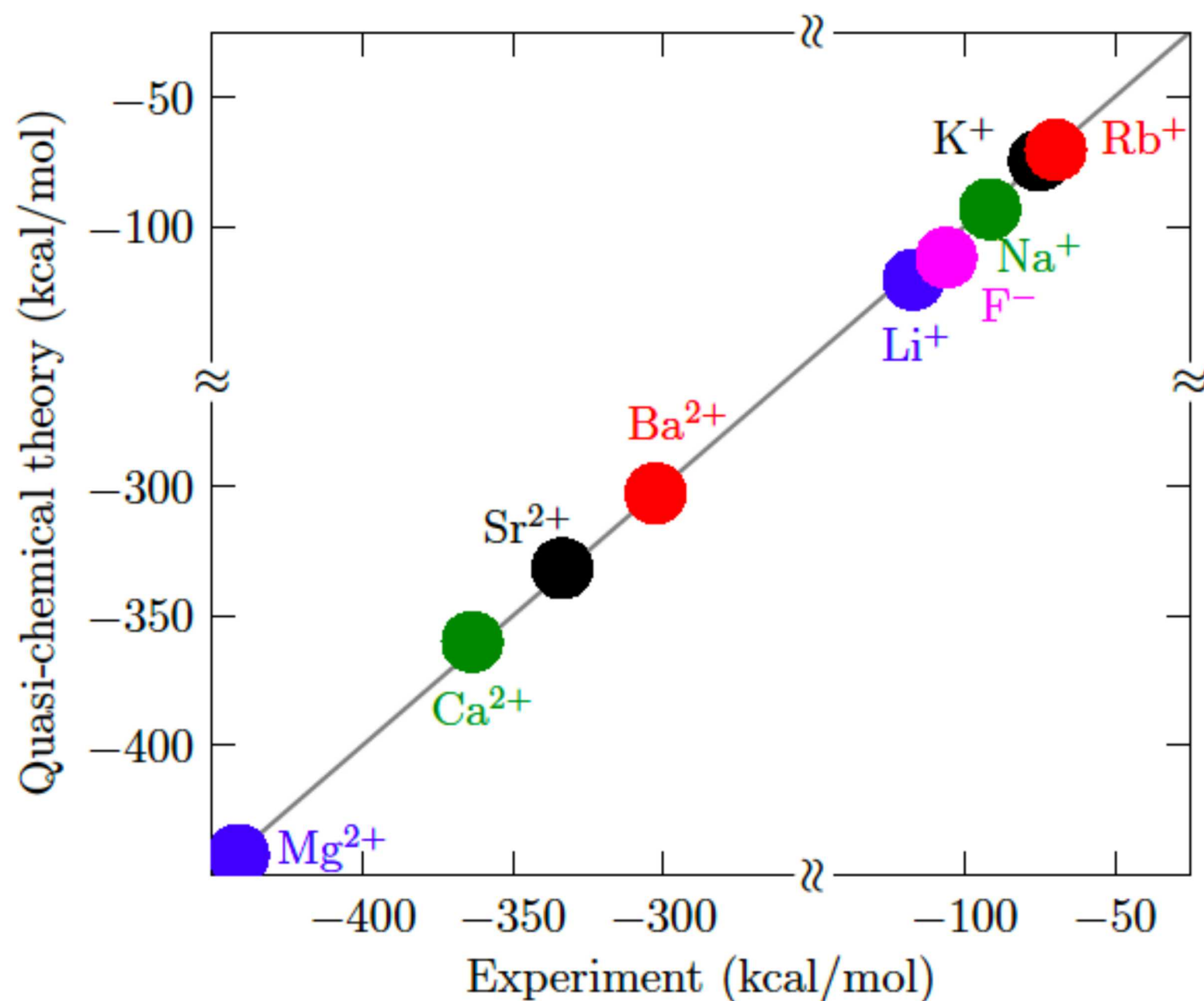
Polarizable Continuum

Polarizable Continuum

Gas-phase DFT



Free energies: DFT + PCM



Best functionals for Na⁺
enthalpy & free energy:

CAM-B3LYP, B3LYP, ...

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Lawrence Pratt (Tulane)

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Questions?



Balloon fiesta, Albuquerque

Ion-water interactions dominate

Table 2. Decomposition of the Binding Energy of the $\text{Na}^+ \cdot (\text{H}_2\text{O})_4$ Cluster^a

method	$\langle E_{\text{iw}} \rangle$	$\langle E_{\text{ww}} \rangle$	$\langle E_{\text{iww}} \rangle$	$\langle E_{\text{www}} \rangle$	remainder	total ΔE
B3LYP	-25.2	1.6	1.5	-0.2	5.8	-77.2
CAM-B3LYP	-26.1	1.6	1.6	-0.1	4.8	-80.8
B97-D	-24.8	1.3	1.6	-0.1	5.1	-77.1
ω B97X	-24.7	1.5	1.4	-0.1	5.6	-76.2
ω B97X-D	-24.4	1.5	1.4	-0.1	5.8	-74.8
B98	-25.0	1.4	1.6	-0.1	5.4	-77.0
PBEPBE	-24.8	1.3	1.7	-0.1	5.2	-76.4
LC- ω PBE	-25.2	1.6	1.5	-0.2	6.2	-76.8
CCSD	-24.4	1.3	1.4	-0.1	8.5	-73.8
CCSD(T)	-24.2	1.2	1.4	-0.1	8.3	-73.3